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Low energy electron attachment to condensed formic acid

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Abstract

Dissociative electron attachment to formic acid in the condensed phase is studied using improved mass spectrometric detection of the negative ion fragments. The desorbed yields are measured as a function of incident electron energy in the range between 3 to 20 eV. Unlike previous work, the formation of the dehydrogenated anion $HCOO^-$ is observed and the signal to noise ratio is much higher for all other ions detected, i.e. OH^-, O^- and H^-. Resonant structure seen in all anion yield functions, is attributed to dissociative electron attachment (DEA), whereas above 14 eV nonresonant dipolar dissociation (DD) dominates the desorption yields.

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Introduction

Formic acid contains a commonly found structural feature with many complex molecules, namely the carboxylic group -COOH, it can thus serve as a model system. It is therefore of interest in many areas of physics and chemistry, more specifically in the fields of astrophysics and biochemistry. The molecule's presence of formic acid in interstellar clouds was discovered by means of micro-wave rotational transitions, in emission towards the galactic center source of Sagittarius B2 [1,2,3,4]. Traces of this simplest organic acid have also been detected in the coma of the Hale-Bopp comet [5,6] and in massive star forming regions [7,8,9,10,11]. In addition to these exciting occurrences in observational astronomy, formic acid plays a significant role in many biochemical processes and is a building block of various natural products. Thus, the interaction of low energy electrons (LEE) with condensed formic acid can be of particular interest in the understanding of radiation induced chemistry both in the interstellar medium and in biological systems. It has been already found that DNA damage by LEE, involves electron capture by a particular DNA components followed by the decay into dissociative electron attachment (DEA) and other dissociative channels [12]. Moreover, the common feature in the DEA cross sections of formic acid and some selected amino acids was attributed to the attachment into the –COOH π^* orbital, but very recently also the evidence of direct attachment to the lowest σ^* orbital was reported [13].
There are many recent experimental studies concerning DEA to the monomeric [14,15,16,17,18,19] and cluster [20] forms of formic acid in the gas phase. Those studies have shown the formation of negative fragment ions i.e. $HCOO^-$, OH^-, O^- and H^- in the electron energy range of 0-15 eV. Moreover, the formation and desorption of the H^-, O^-, OH^- ions from condensed HCOOH was also reported previously [21]. The ion yield of the H^- ion recorded as a function of the electron energy exhibited a broad resonant structure located around 9-10 eV. The similar ion yield functions for H^-, regarding to the shape and the position of maximum of the peak, have been observed from larger organic acids in their condensed phase, e.g. acetic acid (CH_3COOH) [22]. Measurements of the desorption of hydrogen/deuterium ions from isotopically labeled acetic acid molecules showed a more efficient production of H^-/D^- from the acid group –COOH(D) than from the methyl group - CH_3/ CD_3. Generally, the desorption of heavier mass anions is not observed due to their typically having insufficient kinetic energy to overcome the attractive polarization and image-charge forces induced in the molecular film close to the metal substrate. In the present study, by utilizing a modified system for the detection of ions not only ions desorbed with sufficient kinetic energy can be detected but also heavier ions formed on the surface of the multilayer film of formic acid.

Experimental setup

The present data were recorded with a new type of electron stimulated desorption apparatus which will be described in more details elsewhere [23]. The experiments were carried out in a stainless steel ultrahigh vacuum chamber, ion pumped to a base pressure of 5×10^{-10} Torr. Pure formic acid films are formed by condensation directly onto a clean polycrystalline Pt substrate cooled to 15 K by a closed cycle He compressor. The temperature is monitored by an Ag-Ni thermocouple attached to the cold tip of the cryostat. The Pt substrate consists of a 2.0 x 1.0 cm^2 foil of 0.0075 mm nominal thickness and having a purity of 99.95% (Goodfellow Cambridge Limited). The foil can be cleaned by resistive heating to 900 K. A gas-handling manifold consists of two gas or vapor sources connected through bypass and precision leak valves to a small volume. The absolute pressure in this volume is measured with a barometer. Known amounts of gas or vapor are leaked into the analysis chamber by monitoring the differential pressure drop in this volume. The latter is connected via an admission valve to stainless steel capillary (a 2 mm inside diameter) which ends approximately 15 mm from the surface of the Pt. The details of the volumetric dosing procedure have been described previously [24]. A film thickness,

determined by this method, has an uncertainty of about ± 30% with overall repeatability of ± 0.2 monolayer (ML). Formic acid was obtained from Sigma-Aldrich with a stated purity of 98 %. The acid was additionally degassed by repeated freeze-thaw cycles carried out while pumping.
The sample films were bombarded with a 3-20 eV pulsed electron beam of about 3 nA time-averaged current that was produced by a Kimball Physics ELG-2 electron gun. Electrons impinged onto the sample in the horizontal plane at an incident angle of 45° with respect to the surface normal and were focused into a 1 mm^2 spot from a 20 mm working distance (as measured at an incident energy of 10 eV). The absolute electron energy scale of the incident beam was calibrated by taking 0 eV as the onset of the current transmitted at the platinum surface, with an estimated error of about ± 0.3 eV. The electron gun with pulse capability (rise/fall time ~ 10 ns, pulse width ~ 20 ns to 100 μs) is synchronized with the sweep counter of a time of flight (ToF) mass analyzer so that mass spectra can be measured at different incident electron energies. The anion detection is achieved by applying a negative potential pulse (-2 kV, rise/fall time 30 ns, pulse width of 2 μs) applied to the Pt substrate within a short time (~ 10 ns) after the end of each pulse of incident electrons. Desorbed ions are propelled into the entrance optics of a Reflectron ToF mass analyzer (Kore Technology R-500) positioned along the surface normal, at 10 mm from the sample surface. Such an experimental set up allows ions to be detected with high sensitivity, while inflicting a minimum amount of damage to the condensed molecular film.

Results

LEE can initiate molecular fragmentation by either ionization, excitation, or electron attachment to the molecules. It is generally accepted that the basic mechanisms responsible for the formation and desorption of negative ions following low energy electron impact on thin molecular films can be related to elementary process known from gas phase studies, namely dissociative electron attachment (DEA) and dipolar dissociation (DD) [25]. DEA is initiated by the resonant attachment of an electron to a molecule which leads to the formation of a transient negative ion $(TNI)^{\#-}$. The latter may either stabilize, autodetach the electron, or decay into negative ion and neutral (radical) fragments.
In the present experiments the following DEA reaction channels would seem to operate in the electron energy range from 3 to 20 eV:

$$e^- + HCOOH \rightarrow (HCOOH)^{\#-} \rightarrow H^- + HCOO \quad (1a)$$
$$\rightarrow O^- + H_2CO \quad (1b)$$
$$\rightarrow OH^- + HCO \quad (1c)$$
$$\rightarrow HCOO^- + H \quad (1d)$$

Ion yields as a function of incident energy for all desorbed ions are presented in Figs 1-4, respectively, and the positions of all resonances observed are listed in Table 1.

	Peak positions (eV)		
H^-	9.5		
O^-	10.0	13.5	17.5
OH^-	11.3	17.5	
$HCOO^-$	12.7	17.2	

Table 1. Electron energy position (in eV) of resonances for all observed fragment anions formed via DEA to formic acid.

The strongest signal is that of H^- desorption represented by channel (1a). The ion yield function in Fig. 1 shows an intense H^- signal peaking at 9.5 eV, similar to that observed in the previous measurement [21], whereas, two features were observed, a main peak at 7.3 and a shoulder at about 9 eV in the H^- yield in the gas phase [18]. The formation of the H^- ion can be attributed to a core excited resonance, which involves an electronically excited species with two electrons in usually unoccupied molecular orbitals. There are two possible sites in the formic acid molecule from which H^- can be desorbed via dissociation of O-H or of C-H bonds. Both channels are also thermodynamically available at energy thresholds of 3.79 and 3.43 eV, respectively [18]. In the present experiment the appearance energy for H^- is found to be about 5 eV, within the limit of the energy resolution. Despite the fact that experiments were undertaken with two isotopically labeled molecules, i.e. HCOOD and DCOOH, no particular selectivity has been observed, mainly due to strong hydrogen/deuterium scrambling prior to dissociation [21].

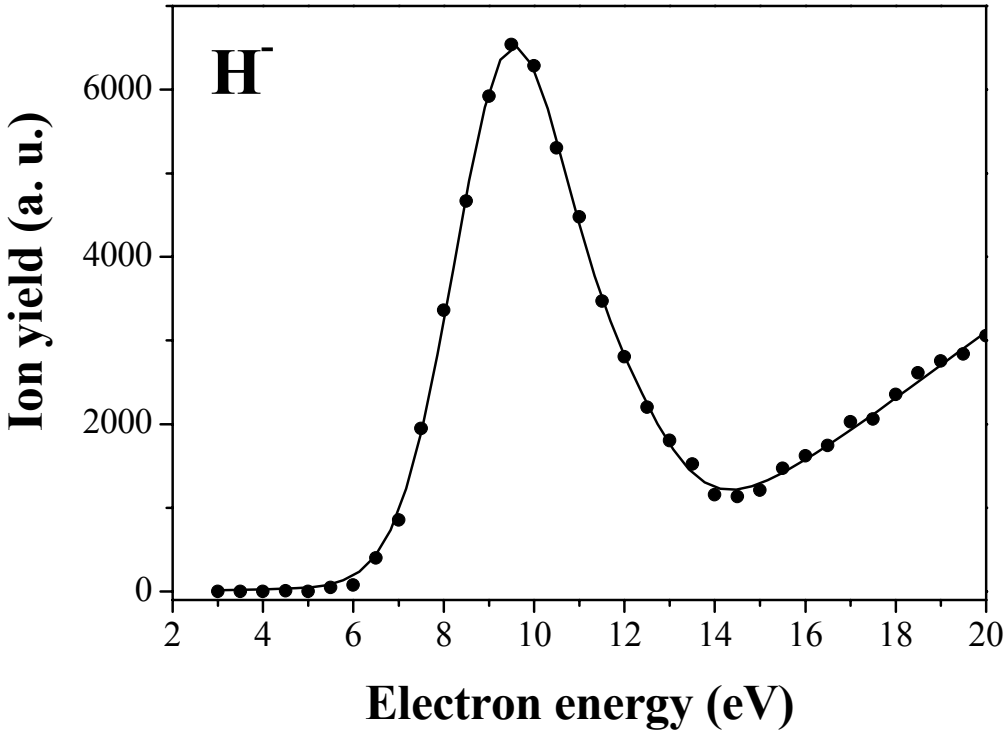

Fig. 1. The hydrogen (H^-) ion yield function from a formic acid film measured in the electron energy range between 3 to 20 eV.

The formation of the O^- ion via reaction (1b) is also thermodynamically possible with a threshold of 3.84 eV [14]; however, the signal detected for that ion has been observed as very weak from HCOOH in both the gas phase [14,18] and the condensed phase [21]. The ion yield detected in the latter case showed two features located at about 10 and 17 eV, similar to those observed here (Fig. 2). However, the previous study [22] also showed that this O^- signal evolved during irradiation and that a O^- signal could not be detected from a freshly deposited sample of HCOOH. Therefore, it was concluded that the

O^- signal derived from DEA to an irradiation product, likely CO_2 [21]. Due to this fact, O^- desorption will not be further discussed.

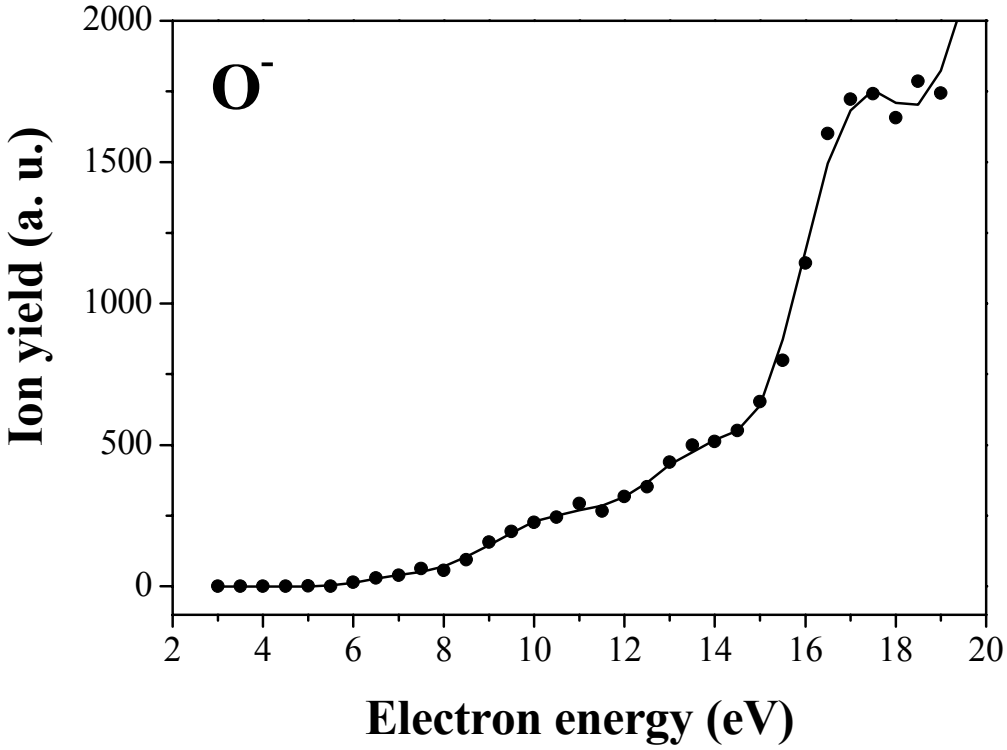

Fig. 2. The oxygen (O^-) ion yield function from a formic acid film measured in the electron energy range between 3 to 20 eV.

Fig. 3 presents the OH^- ion desorption yield as a function of incident energy obtained from the formic acid film. The strongest OH^- desorption signal is obsrved between 9 and 13 eV, where a broad resonant structure is observed, as in the previous experiment [21], but with a much larger signal-to-noise ratio. The gas phase studies [14,18] also showed the formation of the hydroxyl anion for HCOOH, but at much lower energy, i.e. around 7.5 eV with an estimated thermodynamic threshold of 3.48 eV and the simultaneous generation of the HCO radical. In all cases presented in Figs. 1-4, the anion signal observed in the yield function above 15 eV is principally due to the DD process.

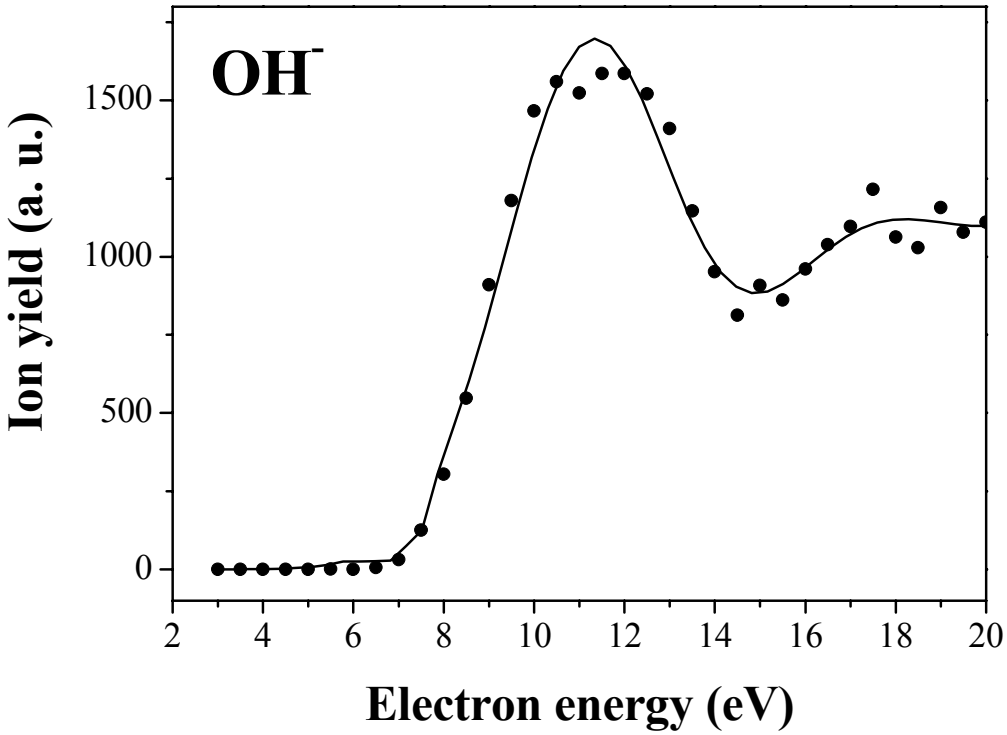

Fig. 3. The hydroxyl (OH^-) ion yield function from a formic acid film measured in the electron energy range between 3 to 20 eV.

Previous studies on anion desorption from formic acid has not shown any $HCOO^-$ signal, however authors have noticed that the reaction channel (1d) could be possible also in the condensed phase, but probably is suppressed by insufficient kinetic energy of that fragment to overcome the polarization force [21]. In the present work, due to the higher sensitivity, the signal of the dehydrogenated anion of formic acid is detected as a function of electron energy (Fig. 4). The $HCOO^-$ ion yield shows two resonant structures near 12.5 and 17.5 eV. In contrast to this high energy process observed in the condensed phase, the formyloxyl anion ($HCOO^-$) formed via DEA to formic acid in the gas phase hasits highest yields at low energy with a resonance maximum located at 1.25 eV [14,18,20]. Due to the considerable electron affinity of the HCOO radical (3.5 eV) electron capture at 1.25 eV forming the dehydrogenated anion occurs via a shape resonance, with the extra electron occupying the lowest orbital of π^* character and localized on the COOH group [20]. Gas phase studies on DEA to different isotopically labeled molecules of formic acids (i.e. HCOOD and DCOOH) showed a dehydrogenation reactions, where abstraction of neutral H or D is exclusively observed from O-H and O-D site, respectively [20].

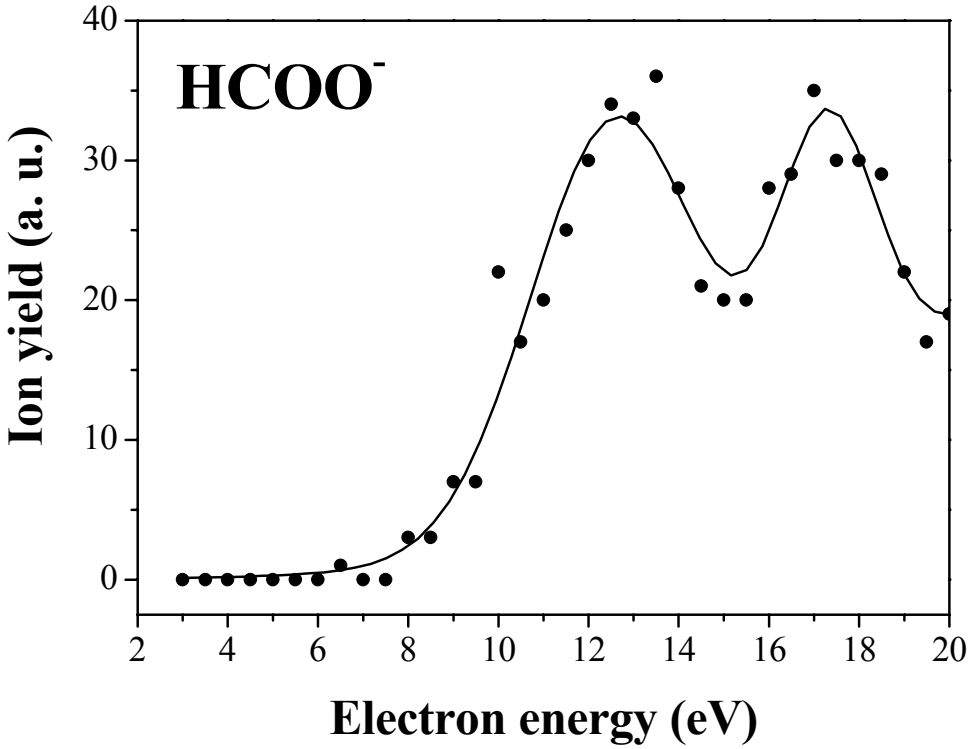

Fig. 4. The formyloxyl ($HCOO^-$) ion yield function from a formic acid film measured in the electron energy range between 3 to 20 eV.

In conclusion, we have presented the results of an investigation on dissociative electron attachment to condensed phase formic acid performed with a new apparatus having a higher sensitivity for condensed phase studies of electron-induced ion desorption than previously available. This advance in the technique allows more different types of desorbed anions to be detected with a higher signal to noise ratio [23]. As an example, we have shown that the present system could easily record the yield function of the dehydrogenated ion $HCOO^-$ desorbing from condensed formic acid, which was previously undetected in similar experiments. The yields of $HCOO^-$ and all other fragment anions recorded as a function of the incident energy in the range between 3 to 20 eV are due to the core excited resonance dominated DEA and DD processes. For the first time, the formation of the dehydrogenated ion $HCOO^-$ is observed in the condensed formic acid. Since formic acid is the simplest model biosystem and due to electron controlled functionalization this study may be considered to be important to understand electron induced damage to more complex biomolecules.

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